TECHNICAL REPORT ARCSL-TR-77069

INFRARED ABSORPTION SPECTRA ATTRIBUTED TO ION-NUCLEATED WATER CLUSTERS

12

by

Hugh R. Carlon

Research Division

September 1977



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

Approved for public release; distribution unlimited.

6110:=

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Dive Enter

Particular de la contraction d		
REPORT DOCUMENTAT	ION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
I. REPORT NUMBER	2. GOVT ACCESSION NO.	
ARCSL-TR-77059		(C)
		TYPE OF REPORT, & PENIOD COVERED
4. TITLE (and Subtitle)	Contract of the second	Technical Report
INFRARED ABSORPTION SPECTRA	ATTRIBUTED /	August 1976-June 1977
TO ION-NUCLEATED WATER CLUS	TERS /	<u> </u>
and the second second		ST PERFORMING ORG. REPORT NUMBER
7. AUTHOR(e)		B. CONTRACT OR GRANT NUMBER(*)
- No Horde		b. CONTRACT ON GRANT NUMBER(*)
Hugh R. Carlon		
and the second second		
9. PERFORMING (RGANIZATION NAME AND ADD	0000	10 DOCCOM CLEVENT ODOLECT TACK
6	, e	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Director, Chemical Systems Laboratory	,	. ILIR
Attn: DRDAR-CLB-PO		; ILIK
Aberdeen Proving Ground, Maryland 2	1010	
11. CONTROLLING OFFICE NAME AND ADDRESS	(1)	12. REPORT DATE
Director, Chemical Systems Laboratory	(//)	September 1977
Attn: DRDAR-CLJ-R	<u></u>	13: NUMBER OF PAGES
Aberdeen Proving Ground, Maryland 2	1010	26
14. MONITORING AGENCY NAME & ADDRESS(IL di	flerent from Controlling Office)	15. SECURITY CLASS. (of thie report)
	101	UNCLASSIFIED
1 (12) 7	_0c1	
\ \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	- F. I	15. DECLASSIFICATION/DOWNGRADING
		NA NA
Approved for public release; distribution	n unlimited	
Approved for public felease, distribution	m uniumtea.	
17. DISTRIBUTION STATEMENT (of the abstract on	tered in Etack 20 If different for	- Panari)
DISTRIBUTION STATEMENT (OF the abstract wi	nered in Discr 20, it different in	ui Reporty
18. SUPPLEMENTARY NOTES		
OF BUTTE EMERITARI ROTES		
19. KEY WORDS (Continue on reverse side if necess	en and Identify by black symbol	
l • a • a ` -	lusters, water	
	aturation ratio	Polymolecular clusters Liquid phase
	iquid droplets	Vapor phase
	tmospheric infrared abso	vapor phase
	lusters	Bulk water phase
		_
20. ABSTRACT (Continue on reverse ship if necesses		
(U) Until recently, it was assumed	that atmospheric was	ter was found in one of three
phases: vapor (monomer), liquid droplets or ice crystals. Now it is known that an ion-nucleated,		
polymolecular cluster phase of water exists in the vapor phase, as well. These water clusters		
consist of numbers of water molecules gathered about small ionic nuclei, where the number of		
molecules per cluster is dependent upon relative humidity and other meteorological parameters.		
dependent upo	ou resente timinatty and	other meteorological parameters.
(Co	ontinued on Reverse Side	2)
1	Diu	

DO 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE UNCLASSIFIED

VIOLASSIFIED

VIOLASSIFICATION OF THIS PAGE (When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. ABSTRACT (Continued)

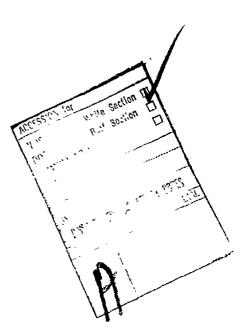
In real atmospheres, mean cluster sizes range from about 11 to about 14 molecules per cluster. Their infrared absorption is due to intermolecular hydrogen bonding, and the "continuum"-like absorption spectrum which they produce is shifted in wavelength by changes in mean cluster size. Water clusters are always present in the atmosphere and in the cleanest of laboratory experimental equipment. Except under supersaturations of about 420% relative humidity, clusters are not able, because of equilibrium considerations, to attain "critical" size and to grow to droplets. Water cluster theory and equations give excellent agreement with observed data for infrared "continuum" absorption.

UNCLASSIFIED

PREFACE

The work described in this report was authorized under In-House Laboratory Independent Research. This work was started in August 1976 and completed in June 1977.

Reproduction of this document in whole or in part is prohibited except with permission of the Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010; however, DDC and the National Technical Information Service are authorized to reproduce the document for United States Government purposes.



SUMMARY

The spectrum is presented of anomalous infrared absorption attributed to ion-nucleated water clusters in vapor-saturated air. The absorption is anomalous in the sense that it cannot be accounted for by water vapor or liquid water droplets. The spectrum was taken by emission, from a 3.05-m path length of cooling, saturated steam at 32.5°C. Relationships between mean cluster size, (c)_{mean}, saturation ratio, (s), and wavelength shift of the spectrum are developed. The wavelength shift continues into the bulk liquid phase of water as well, where (c)_{mean} is determined primarily by the purity of the liquid water sample. It is concluded that the momalous infrared absorption in real atmospheres is attributable to ion-nucleated, polymolecular water clusters of size $11 \le (c)_{mean} \le 14$. Practical applications of these findings are discussed in this paper. A first composite of water cluster absorption spectra is constructed for the infrared wavelength region from 2 to 24 μ m, for a variety of vapor-phase and liquid-phase conditions.

CONTENTS

		Page
I.	INTRODUCTION	9
11.	EMISSION/ABSORPTICN SPECTRUM ATTRIBUTED TO WATER CLUSTERS IN AIR	9
III.	RELATIONSHIP BETWEEN (c), (s), AND λ_{max}	12
iV.	THE WATER DIMER	14
V.	A COMPOSITE PICTURE OF WATER CLUSTER INFRARED ACTIVITY	14
VI.	CONCLUSIONS	15
	LITERATURE CITED	19
	GLOSS ARY	21
	DISTRIBUTION LIST	23

INFRARED ABSORPTION SPECTRA ATTRIBUTED TO ION-NUCLEATED WATER CLUSTERS

I. INTRODUCTION.

In an earlier paper 1 we presented experimental infrared emission spectra of steam in the 7- to 13- μ m wavelength region. These spectra showed anomalous emission which we attributed to tiny water droplets that were too small to produce noticeable optical scattering in the visible wavelengths. The spectra exhibited wavelength shifts with heating or cooling. Because instrumentation was not available, it was impossible to characterize the aerosols present in those trials.

As part of recent work in aerosol spectroscopy² we were able to perform similar experiments with condensing steam in which the aerosol was completely characterized. Operating under conditions of radiometric null at maximum radiometer gain settings, we have repeatedly observed a spectral feature in warm air saturated with water vapor which cannot be attributed either to water vapor or to water droplets. These recent experiments were designed so that a saturation ratio. (s), = 1.0 was maintained cs residual steam clouds in a test chamber with a 3.05-m optical path were permitted to cool gradually and to dissipate. After careful corrections were made for spectral absorption/emission by water vapor or by residual droplets,³ the anomalous spectral feature remained in almost all trials. In thermal equilibrium, the observed anomalous emission had radiant emittance values three to four times higher than the combined emittances of water vapor and residual droplets present in the test chamber. In earlier papers, the radiometer¹ was described and the experimental test chamber arrangement and procedure² were discussed.

II. EMISSION/ABSORPTION SPECTRUM ATTRIBUTED TO WATER CLUSTERS IN AIR.

Figure 1 shows the absorption spectrum of the anomalous feature as we observed it in the 8- to 13- μ m wavelength region for the experimental conditions, namely, air temperature, (θ_k) , = 305 5°K and saturation ratio, (s), = 1.0. Each hollow point in figure 1, depending upon wavelength, averages 6 to 9 experimental data points. The vertical error bars for these representative data enclose the maximum excursions of any experimental data points at each wavelength. The horizontal error bars indicate the radiometer wavelength resolution, which was 2% of center wavelength. The values of the anomalous absorption coefficient, $(\alpha_c)_{\lambda}$, (m^2/gm) shown in figure 1 are used in equation 1:

$$ln(1/T_{\lambda}) = (\alpha_c)_{\lambda} (C_c) (L_m)$$
 (1)

where

是一个人,我们就是一个人,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是 第一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们就是一个人的,我们

 C_c = the concentration of the anomalous species (gm/m³)

 $L_{\rm m}$ = the optical path length (3.05 m in the present experiments)

 T_{λ} = the infrared transmittance at wavelength, λ , (μ m)

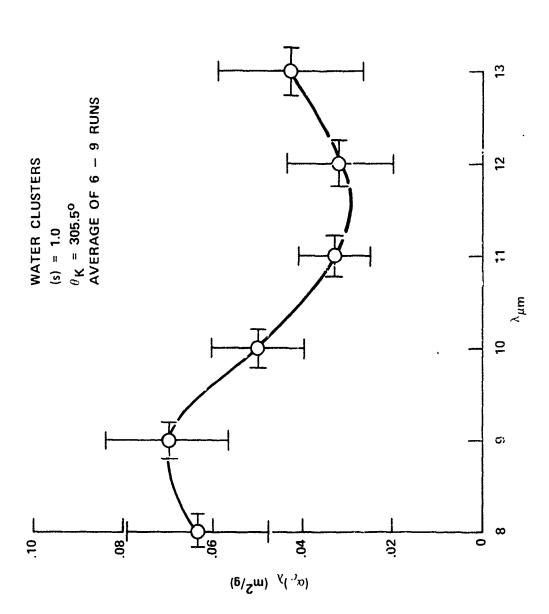


Figure 1. Infrared Absorption Spectrum Attributed to Water Cluster in Vapor-Saturated Air

Since, in the course of these experiments, we did not know the precise nature of the phase-transitional species present in our chamber (which accounted for the anomalous absorption), the determination of C_c was difficult because represented in this concentration were species which were neither vapor nor liquid. A simpler procedure would have been to combine $(\alpha_c)_{\lambda}$ and C_c into a single absorption coefficient with reciprocal length units. To do this however would have eliminated the opportunity to study changes in the spectral behavior of the species with experimental parameters, especially (s). Since we had already observed evidence of wavelength shifts in anomalous emission spectra of steam under varying saturation ratios, we decided to work with $(\alpha_c)_{\lambda}$ and C_c separately, as is our custom in aerosol spectroscopy.² The calculation of quantitative values of $(\alpha_c)_{\lambda}$ involved a determination of the water present in excess of that present as either vapor or liquid aerosol droplets larger than about 0.1μ . It will become apparent in the following discussion that the $(\alpha_c)_{\lambda}$ shown in figure 1 is in reasonably consistent agreement with observed data, but that the shape of the spectrum in figure 1 probably is more important than its absolute amplitude, at least for the present work.

Water clusters are the phase-transitional species between water vapor and liquid water droplets in the absence of "foreign" condensation nuclei. However, as C. T. R. Wilson^{4,5} showed in his classical cloud chamber work, later lucidly summarized by J. G. Wilson,⁶ water clusters in real atmospheres are not able to grow large enough to reach stable size except in the presence of vapor supersaturations of at least about (s) = 4.2 (i.e., 420% RH), for standard starting conditions of temperature and pressure. As stated by J. G. Wilson, he critical diameter for droplet formation corresponds to a cluster size or count (c = water molecules/cluster) of about 30. Thus, in real atmospheres we are given a picture of water clusters of statistical size distributions with "tails" extending from (c) = 2 to (c) = 30 but with statistical mean values of (c) somewhere in between, co-existing with a bewildering array of "foreign" condensation nuclei, and with the whole lot dependent for average cluster or droplet size primarily upon meterorological parameters, especially the saturation ratio, (s).

是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人,我们是一个人

We know also that water clusters can be nucleated in two ways: on ions, or by homogeneous nucleation. McDonald's papers^{8,9} on homogeneous nucleation of water vapor are classics, and Abraham¹⁰ has given an excellent presentation of this subject. But in applying their data⁸⁻¹⁰ to the real atmosphere case which we were considering, we found that homogeneous nucleation of water clusters did not satisfy our observed results for two reasons:

- 1. The expected mean value of cluster count (c) for homogeneously nucleated water clusters is zero, not somewhere between 2 and 30 depending primarily upon the value of (s) as will be seen to be necessary in the present discussion.
- 2. The numbers and mass fractions of water clusters predicted by homogeneous nucleation theory are not nearly large enough to account for the observed infrared spectral effects.

Thus, in the balance of this paper we shall attempt to show that figure 1 depicts the infrared spectrum of water clusters in air, of cluster sizes (c) between 2 and 30, distributed about some mean value of (c), and corresponding to the case where (s) = 1.0 and (θ_k) = 305.5° K. Furthermore, we shall attempt to show that these water clusters are formed on *ionic nuclei*.

III. RELATIONSHIP BETWEEN (c), (s), AND λ_{max} .

The literature contains many references pertaining to the growth of water clusters on ionic nuclei in equilibrium with various saturation ratios, (s). The work of Castleman and Tang¹¹ is perhaps best known. The lower curve of figure 2 shows results obtained by these workers relating mean molecule counts, (c), of water clusters formed on lead ion, (Pb+), for various values of (s). J. G. Wilson⁷ indicated that the sign of the ion will affect (c):(s) equilibria, with negative ions being favored in the case of water. In addition, results of other workers 12,* indicated that when ionically nucleated in typical vapor-saturated air (s) = 1.0 for $273^{\circ} \le \theta_k \le 373^{\circ} K$, mean water cluster sizes in air of between (c) = 11 and (c) = 17 were found. Thus, in figure 2 an upper curve is drawn, nearly parallel to the lower curve of Castleman and Tang's data, 11 but for substantially larger values of cluster size, (c), corresponding to given (s) values. The left-hand end of the upper curve in figure 2 is drawn through a point which can be determined from the absorption spectrum of water vapor [i.e., monomer, (c) = 1] by a lengthy calculation. (This will not be presented here.) In this discussion, the precise relationship between the mean size of water cluster distributions found in real atmospheres and saturation ratio is relatively unimportant at this point. Since the upper curve of figure 2 is probably representative, we shall use its equations in the subsequent discussion.

(c) =
$$1.2 \ln(s) + 14.2$$
 (2)

(s) =
$$\exp [0.833(c) - 11.8]$$
 (3)

It was mentioned earlier that a wavelength shift occurs in the spectrum of figure 1 with changes in (s). The maximum of $(\alpha_c)_{\lambda}$ at $\lambda_{max} = 9.0 \,\mu m$ moves to the left (i.e., toward higher frequencies) at lower (s) values, and the magnitude of $(\alpha_c)_{\lambda}$ diminishes very rapidly as well. In our chamber measurements, this seemed to give an abrupt loss of emission signal when vapor saturation was lost, usually a few minutes after evaporation of the last visible liquid water droplets. Evidence of this wavelength shift also is found in atmospheric or laboratory infrared spectra of the 8- to 13- μ m wavelength region taken under conditions where (s) is known or can be calculated. In practice, it is found that λ_{max} , the wavelength at which the peak value of $(\alpha_c)_{\lambda}$ is found (as in figure 1), is approximated by

$$\lambda_{\text{max}} = 2.41 \sqrt{c} \tag{4}$$

and since (c) can be calculated from (s) if their relationship is known, as for example from equation 2, it is possible to relate λ_{max} to both mean cluster size (c) and to (s) with which (c) is in equilibrium. For example, at (s) = 0.1 (10% RH), $(\alpha_c)_{\lambda}$ will have shifted its peak to $\lambda_{max} = 8.15 \ \mu m$ from 9.0 μm at (s) = 1.0.

^{*} Harden, C. S. Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010; private discussions on charged water cluster size distributions as functions of saturation ratio based upon quadrapole mass spectrophotometric measurements, July 1976.

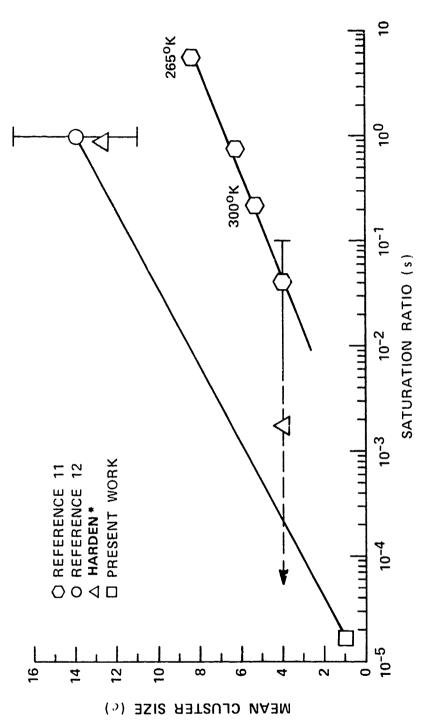


Figure 2. Relationship Between Mean Cluster Size and Saturation Ratio for Water Clusters in Air

Upper curve — data taken from papers of Potter and Hoffman, 12 from Harden,* and from present work.

Lower curve - data taken from paper of Castleman and Tang, 11 for (Pb⁺) ions.

Harden, C. S. Chemical Systems Laboratory, Aberdeen Proving Ground. Maryland 21017; private discussions on charged water cluster size distributions as functions of saturation ratio based upon quadrapole mass spectrophotometric measurements, July 1976.

IV. THE WATER DIMER.

The few attempts which have been made to relate atmospheric infrared absorption to water clusters have involved the water dimer, i.e., the cluster of size (c) = 2. Varanasi, et al. 13 reported unusually high, or anomalous, water "vapor" absorption coefficients near 10 - μ m wavelength with inverse temperature dependency which was considered by Bignell 14 and others, 15 possibly to be explained by the presence of the water dimer. Presumably, the equilibrium considered in moist air was

$$2 H_2O \rightleftharpoons (H_2O)_2 \tag{5}$$

where the equilibrium constant is very small and the expected value is near zero. Ionic nucleation is not considered in equation 5. Rather, the "nucleation," if it can be so called, is of the homogeneous type. We have shown earlier that homogeneous nucleation almost certainly is not the mechanism of water clustering responsible for infrared activity observed in the open atmosphere. As for ionic nucleation, (c) = 2 is the expected value only for extremely low values of (s). Thus, in the context of the present discussion, the dimer is but a small contributor to infrared absorption on the low-(c) "tail" of a statistical distribution of absorbing clusters centered on some mean value of (c) determined primarily by (s). In real atmospheres, from the equations presented here, a reasc table approximation is:

$$11 \leq (c)_{\text{mean}} \leq 14$$
.

A COMPOSITE PICTURE OF WATER CLUSTER INFRARED ACTIVITY.

We hypothesize at the outset of this section that the physical phase in which water clusters are found seems to have little effect upon their infrared spectra. The relationships between broad, continuum-like infrared absorption band wavelength shifts and solute ion concentrations in liquid water solutions are well documented 16 if not fully understood. Clearly, these ion concentrations affect complex refractive index measurements even of "pure" water, especially the imaginary index component.* Using equation 4, it was possible to predict, with reasonable agreement, the location of λ_{max} for the absorption peak due to water clusters of larger mean size which are found in the liquid, as compared to the vapor phase. λ_{max} is found near 14 µm in infrared spectra of reasonably pure liquid water films (hopefully uncontaminated by ions from salts used to fabricate sample cell windows), corresponding to mean cluster sizes of about (c) = 34 molecules per average water cluster formed on available ionic nuclei at any given instant in bulk liquid water samples. Other lesser cluster absorption maxima are found near 6.9-μm and 4.7-μm wavelengths in "pure" water film spectra. They, too, change or shift wavelength with solute ion concentration and, hence, with mean cluster size. Their behavior can be described by equations that have the form of equation 4, but with suitably adjusted coefficients.

Querry, M. R. University of Missouri, Kansas City, Missouri; private discussions of refractive index measurements of water-containing liquid solutions, in the infrared. March 1977.

From all available information we were able to prepare a tentative, first composite picture of infrared absorption activity by water clusters in air or in liquid water solution. This composite is shown in figure 3. We cannot overemphasize the fact that this figure is intended only as a starting point for subsequent work. The approximations used in its preparation were of first order only, and it would be most fortuitous if subsequent work confirmed any degree of precision in these primarily calculated curves.

Nevertheless, figure 3 does contain a great substantial amount of "hard" data. To begin with, steam turns out to be a nearly ideal medium for the study of infrared absorption effects of water because both the vapor and liquid phases are present under vapor saturation conditions and at high vapor pressures. Initially, recondensation of steam droplets produces rather pure liquid water droplets, and thus the shift of λ_{max} (equation 4) of the continuum absorption is accomplished smoothly between physical phases. Potter and Hoffman¹² found not only anomalous infrared emission in this phase transition at 100°C, but apparent luminescence (i.e., nonthermal behavior) as well, which they attributed to water clusters. Good in frared absorption coefficient, $(\alpha)_{\lambda}$, spectra of water vapor (monomer) and liquid water films also are available from many sources, including our own measurements. Wavelength shifts with specific solute concentrations in the liquid phase are known (e.g., for HCl, 16 used as data points in figure 3). A portion of the curve passing through the "phase change" point of figure 3 is the spectrum of figure 1. Shapes of the curves in the vapor phase are known from atmospheric and laboratory infrared spectra of anomalous water "continuum" absorption, e.g., as summarized by Roberts, et al. 17 The wavelength shift in the vapor phase can be deduced from water vapor spectra where (s) is known.¹⁸ While specific points in figure 3 corresponding to various (s) and (c) values in the vapor phase can only be estimated from figure 2 and equations 2 and 3, the 'imiting values of $(\alpha_c)_{\lambda}$ for the monomer (vapor), and its wavelength spectrum, are known.

The development presented in this paper can be extended to include equations relating water cluster absorption to anomalous atmospheric infrared "continuum" absorption which has proven to be very troublesome to modelers of atmospheric transmission and its prediction, especially in the 7- to 13- μ m atmospheric window region. Bignell¹⁴ and others have call this "e-type" absorption. Infrared continuum absorption by atmospheric water will be devoted specifically to that subject.

VI. CONCLUSIONS.

We conclude that:

1. Figure 1 is very probably the infrared absorption spectrum of the statistical distribution water clusters found under atmospheric pressure at saturation humidity (s) = 1.0 and θ_k = 305.5°K. The probable mean cluster size or molecular count at any instant in time is on the order of (c) = 14 (equations 2 and 3). In real atmospheres, the range of mean water cluster sizes is on the order of $11 \le (c)_{mean} \le 14$.

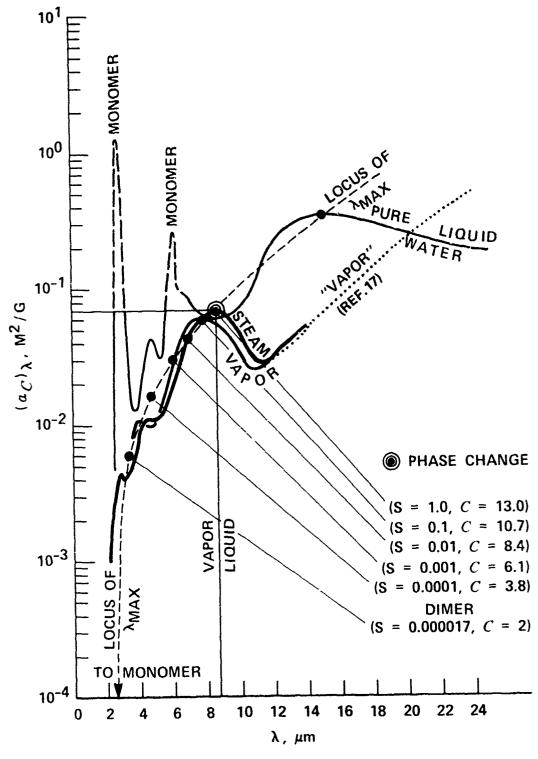


Figure 3. Composite Picture of Water Cluster Infrared Absorption Activity in the Liquid and Vapor Phases, Based Upon Best Current Data

- 2. The wavelength of the maximum value of the absorption coefficient, $(\alpha_c)_{\lambda}$, which is $\lambda_{\text{max}} = 9.0 \ \mu\text{m}$ in figure 1, shifts toward shorter wavelengths (higher frequencies) with decreasing saturation ratio, (s), or with other changes that tend to reduce (s), e.g., increasing air temperature. This wavelength shift can be approximated by equation 4.
- 3. The water dimer equilibrium expressed by equation 5 makes only a vanishingly small contribution to anomalous infrared absorption by atmospheric water.
- 4. Ions in the atmosphere or in liquid water solution are the nuclei for infrared-active water clusters. The finding of Spencer, et al. 19 and others that stable droplet formation and growth can be enhanced by coronal discharges is consistent with this idea. In water solutions, clusters produce continuum-like infrared absorption in liquid water films, especially at longer wavelengths.
- 5. A first composite of water cluster absorption coefficient spectra (figure 3) can be constructed showing the response of $(\alpha_c)_{\lambda}$ to many parameters. This composite can serve as a point of departure for investigations into specific manifestations of water cluster absorption in the infrared, e.g., "e-type" ¹⁴ infrared "continuum" absorption by atmospheric water.

LITERATURE CITED

- 1. Carlon, H. R. Appl. Opt. 10, 2297 (1971).
- 2. Carlon, H. R., Anderson, D. H., Milham, M. E., Tarnove, T. L., Frickel, R. H. and Sindoni, I. Appl. Opt. 16, 1598 (1977).
 - 3. Carlon, H. R., Milham, M. E., and Frickel, R. H. Appl. Opt. 15, 2454 (1976).
 - 4. Wilson, C. T. R. Philos. Trans. 189, 265 (1897).
 - 5. Wilson, C. T. R. Philos. Trans. 192, 403 (1899).
- 6. Wilson, J. G. The Principles of Cloud Chamber Technique. Cambridge Monographs on Physics. The University Press, Cambridge, England. 1951.
 - 7. *Ibid.* p 6. 1951.

是一个人,这个人,这个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是一个人,他们是

- 8. McDonald, J. E. Amer. J. Phys. 30, 870 (1962).
- 9. McDonald, J. E. Amer. J. Phys. 31, 31 (1963).
- 10. Abraham, F. F. Homogeneous Nucleation Theory. Academic Press, New York. New York. 1974.
 - 11. Castleman, A. W., and Tang, I. N. J. Chem. Phys. 57, 9 (1972).
 - 12. Potter, W. R., and Hoffman, J. G. Infrared Physics 8, 265 (1968).
- 13. Varanasi, P., Chou, S., and Penner, S. S. J. Quant. Spectrosc. Radiat. Transfer 8, 1537 (1968).
 - 14. Bignell, K. J. Quart. J. Royal Meteorol. Soc. 96, 390 (1970).
 - 15. Penner, S. S. J. Quant. Spectrosc. Radiat, Transfer 13, 383 (1973).
 - i6. Falk, M., and Giguere, P. A. Canad. J. Chem. 35, 1195 (1957).
- 17. Roberts, R. E., Selby, J. E. A., and Biberman, L. M. Appl Opt. 15, 2085 (1976).
- 18. Aref'ev, V. N., Dianov-Klokov, V. I., Radionov, V. F., and Sizov, N. I. Opt. Spektrosc. 39, 560 (1975).
- 19. Spencer, W. P., Johnson, R. A., and Vietti, M. A. J. Aerosol Sci. 7, 441 (1976).

GLOSSARY

 $(\alpha_c)_{\lambda}$ = absorption coefficient of anomalous infrared absorption attributed to water clusters, m²/gm.

(c), (c)_{mean} = mean number of water molecules comprising water cluster sample in a given instant of time, or cluster size of a given cluster at a given instant, water molecules/cluster.

C_c = concentration of anomalous species considered as water clusters in sample, gm/m³

 L_{m} = optical path length, m.

 λ_{max} = wavelength of peak absorption attributed to clusters, μm .

(s) = saturation ratio (fractional relative humidity) of water in air.

 T_{λ} = infrared transmittance through sample at wavelength, λ .

 θ_{k} = absolute temperature, $^{\circ}$ K.

DISTRIBUTION LIST FOR ARCSL-TR-77059

Names	Copies	Names	Copies
	-	Director	
CHEMICAL SYSTEMS LABORATORY		Defense Civil Preparedness Agency Attn: PO(DC)	1
OFFICE OF THE DIRECTOR	1	Washington, DC 20301	
Attn: DRDAR-CLG	1	Hamiligton, De 2000.	
SAFETY OFFICE	1	CINCUSAREUR	_
Attn: DRDAR-CLF	•	Attn: AEAGC-RSI	1
ERDA SUPPORT OFFICE	1	APO New York 09403	
Attn: DRDAR-CLE PLANS & PROGRAMS OFFICE	-		
Attn. DRDAR-CLR-L	4	Deputy Chief Of Staff for Research,	
Attn. DRDAR-CENE		Development & Acquisition	1
AUTHOR'S COPIES: Research Division	25	Attn: DAMA-CSM-CM	1
AUTHOR'S COLLEGE MODEL TO THE		Attn: DAMA-ARZ-D	1
BIOMEDICAL LABORATORY		Washington, DC 20310	
Attn: DRDAR-CLL	1		
Attn: DRDAR-CLL-M	1	Headquarters, Sixth US Army	
Attn: DRDAR-CLL-MC	1	NBC Office	1
Attn: DRDAR-CLL-MN	1	Attn: AFKC-OP-PN	·
Atm: DRDAR-CLL-V	1	Presidio of San Francisco, CA 94129	
		HOD : (DAMI FIT)	1
CB DETECTION & ALARMS DIVISION	•	HQDA (DAMI-FIT) WASH, DC 20310	
Attn: DRDAR-CLC	1	WASH, DC 20310	
DEVELOPMENTAL SUPPORT DIVISION		CINCUSAREUR	
Atm: DRDAR-CLJ-R	2	Attn: AEAMD-PM	1
Atm: DRDAR-CLJ-L	3	APO New York 09403	
Atm: DRDAR-CLJ-M	1		
Attn: DRDAR-CLJ-P	1	US ARMY HEALTH SERVICE COMMAND	
MUNITIONS DIVISION Attn: DRDAR-CLN	1	Superintendent	
Attn: DRDAR-CLN-D	1	Academy of Health Sciences	
Attit: DRDAR-CERED		US Army	I
PHYSICAL PROTECTION DIVISION		Attn: HSA-CDC	1
Attn: DRDAR-CLW-P	1	Attn: HSA-IHE	•
Atm. District Co.		Fort Sam Houston, TX 78234	
RESEARCH DIVISION		THE STATE OF THE STATE AND	
Atm: DRDAR-CLB	1	US ARMY MATERIEL DEVELOPMENT AND	
Attn: DRDAR-CLB-B	1	READINESS COMMAND	
Attn: DRDAR-CLB-P	1	O managed as	
Attn: DRDAR-CLB-T	1	Commander US Army Materiel Development and	
		Readiness Command	
SYSTEMS ASSESSMENTS OFFICE	1	Attn: DRCDE-DM	1
Atm: DRDAR-CLY-A	1	Attn: DRCLDC	1
		Attn: DRCMT	1
DEPARTMENT OF DEFENSE		Atm: DRCSF-S	1
		Attn: DRCDL/Mr. N. Klein	1
Administrator		Attn: DRCBI/COL Gearin	1
Defense Documentation Center	12	5001 Eisenhower Ave	
Attn: Accessions Division		Alexandria, VA 22333	
Cameron Station Alexandria, VA 22314			
Alexandria, VA 22314		Commander	
Director		US Army Foreign Science & Technology Center	1
Defense Intelligence Agency		Attn: DRXST-CX2	1
Attn: DB-4G1	1		•
Washington, DC 20301		220 Seventh St., NE	
-		Charlottesville, VA 22901	
DEPARTMENT OF THE ARMY		Director	
	•	US Army Materiel Systems Analysis Activity	
HQDA (DAMO-SSC)	1	Attn: DRXSY-D/Dr. Fallin	1
HQDA (DAMA-ARZ)	1	Aberdeen Proving Ground, MD 21005	
WASH DC 20310			

DISTRIBUTION LIST FOR ARCSL-TR-77059 (Contd)

Names	Copies	Names	Copies
Project Manager for XM-1 Systems Office		US ARMY TRAINING & DOCTRINE COMMAND	
Attn. DRCPM-GCM-SW/Mr. R. Slaughter Warren, M1 28150	1	Commandant	
warten, Mi 28130		US Army Infantry School	
Office of the Project Manager for Smoke/Obscurants		Attn: NBC Division	1
Attn: DRCPM-SMK-M	1	Fort Benning, GA 31905	
Aberdeen Proving Ground, MD 21005			
		Commandant	
Commander		US Army Missile & Munitions Center & School	,
US Army Missile Research and Development Command		Attn: ATSK-CD-MD Attn: ATSK-DT-MU-EOD	1
Redstone Scientific Information Center Attn: Chief, Documents	1	Redstone Arsenal, AL 35809	•
Attn: DRSMI-RKL/Dr. W. Wharton	i	,	
Attn: DRSMI-RFG/Mr. B. Fowler	i	Commander	
Redstone Arsenal, AL 35809		US Army Logistics Center	
		Attn: ATCL-MM	i
Director		Fort Lee, VA 23801	
DARCOM Field Safety Activity		Commandant	
Attn: DRXOS-C Charlestown, IN 47111	1	US Army Military Police School/Training Center	
Charlestown, IN 47111		Attn: ATZN-CDM	1
US ARMY ARMAMENT RESEARCH AND		Attn: ATZN-TDP-C	1
DEVELOPMENT COMMAND		Attn: ATSJ-TD-CR	1
		Fort McClellan, AL 36205	
Commander			
US Army Armament Research and Development Comn		Commander	
Attn. DRDAR-TD Attn: DRDAR-TSS	1 1	US Army Infantry Center Attn: ATSH-CD-MS-C	1
Dover, NJ 07801	1	Fort Benning, GA 31905	1
		, and a second s	
US ARMAMENT MATERIEL READINESS COMMAN	D	Commander	
_		HQ, USATRADOC	
Commander		Attn: ATCD-TEC/Mr. M. Pastel	1
US Armament Materiel Readiness Command Attn: DRDAR-ASN	1	Fort Monroe, VA 23651	
Attn DRDAR-SA	1	Director	
Rock Island, IL 61201	•	US Army Training and Doctrine Command	
		Systems Analysis Activity	
Commander		Attn: Code ATAA-TDS/MAJ R. Allen	1
US Army Dugway Proving Ground		White Sands Missile Range, NM 88002	
Attn: Technical Library, Docu Sect	1	Commandant	
Attn. STEDP-MT-DA-E Dugway, UT 84022	1	US Army Ordnance & Chemical Center & School	
Dugway, 01 04022		Attn: ATSL-CL-NB	1
Commander		Attn: ATSL-CL-MS/Dr. T. Wech	1
Rocky Mountain Arsenal		Aberdeen Proving Ground, MD 21005	
Attn. SARRM-QA	1		
Commerce City, CO 80022		US ARMY TEST & EVALUATION COMMAND	
Commonder		Record Copy	
Commander Pine Bluff Arsenal		CDR, APG	
Attn: SARPB-ETA	1	Attn: STEAP-AD-R/RHA	1
Pine Bluff, AR 71611	•	APG-Edgewood Area, Bldg E5179	
Director		Commander	
US Army Ballistic Research Laboratories		US Army Test & Evaluation Command	•
Attn: DRDAR-BLT/Mr. T. Finnerty Attn: DRDAR-BLP/Mr. N. Gerri	1 1	Attn: DRSTE-FA APG-Aberdeen Area	1
Attn: DRDAR-TSD-S	1	TO TOOLOOM LEGG	
Building 328	•		
Aberdeen Proving Ground, MD 21005			

DISTRIBUTION LIST FOR ARCSL-TR-77059 (Contd)

DISTRIBUTION LIST FOR AROUS 1			
Names	Copies	Names	Copies
<u>.</u>		DEPARTMENT OF THE AIR FORCE	
Commander			
US Army Tropic Test Center Attn: STETC-MO-A (Tech Library)	1	HQ Foreign Technology Division (AFSC)	i
Attn: STEIC-MC-A (Tech Library)		Attn: PDRR	1
APO New York 09827		Wright-Patterson AFB, OH 45433	
Commander		Commander	
Dugway Proving Ground	1	Aeronautical Systems Division	
Attn: STEDP-PO	-	Attn: ASD/AELD	1
Dugway. UT 84022		Wright-Patterson AFB, OH 45433	
DEPARTMENT OF THE NAVY		HQ, USAF/SGPR	1
m		Forrestal Bldg	
Commander Naval Explosive Ordnance Disposal Facility		WASH DC 20314	
Attn. Army Chemical Officer, Code 604	1		
Indian Head, MD 20640		Department of Air Force	
Indian Head, MD 20040		Air Staff	
Oden	1	Director of Operations and Readiness	1
Commander Naval Surface Weapons Center		Attn: MAJ Dixon	•
Naval Surface weapons Center		Washington, DC 20310	
White Oak Laboratory Attn: Tech Lib & Info Svcs Br	1		1
Attn: Tech Lin & Into Sves Di		HQ, Ogden ALC/MMWRA	•
Silver Spring, MD 20910		Hill AFB, UT 84406	
a	1		
Commander Naval Intelligence Support Center		Commander	
4301 Suitland Road		Armament Development & Test Center	1
Washington, DC 20390		Attr. DLOSL (Technical Library)	*
washington, DC 20390		Eglin AFR, FL 32542	
Commandat		a warman	1
Commander Naval Surface Weapons Center		NORAD Combat Operations Center/DBN	•
Dahlgren Laboratory		Cheyenne Mtn Complex, CO 80914	
Attn: DX-21	1		
		OUTSIDE AGENCIES	
Dahlgren, VA 22448			
Chief, Bureau of Medicine & Surgery		Battelle, Columbus Laboratories	1
Department of the Navy		Attn: TACTEC	•
Attn. CODE 5	1	505 King Avenue	
Washington, DC 20372		Columbus, OH 43201	
wasnington, DC 20372			1
Commander		Director of Toxicology	•
Naval Weapons Center		National Research Council	
Attn: Code 3311/Mr. R. Bird	1		
China Lake, CA 93555		Washington, DC 20418	
Citilla Lake, Cit 75550			
Commanding Officer		Director	
Naval Weapons Support Center		Central Intelligence Agency	1
Attn. Code 5041/Mr. D. Johnson	1	Attn: ORD/DD/S&T	•
Crane, IN 47522		Washington, DC 20505	
Crane, IIV 4/322		ADDITIONAL ADDRESSEES	
Commander		ADDITIONAL ADDRESSEES	
Naval Research Laboratory		. Commander	
Attn: Code 5709/Mr. W.E. Howe	1	Harry Dismond Laboratories	
4555 Overlook Avenue, SW		Attn: DRXDO-RDC/Mr. D. Giglio	1
Washington, DC 20375		2800 Powder Mill Road	
		Adelphi, MD 20783	
US MARINE CORPS		-	
		Chief, Office of Missile Electronic Warfare	
Commandant		US Army Electronic Warfare Laboratory	1
HQ, US Marine Corps		Attn: DRSEL-WLM-SE 1 Write Sands Missile Range, NM 88002	•
Attn: Code POM-33/MAJ J. F. Nardo		White Sands Missile Range, NM 88002	
Washington, DC 20380			
-			

DISTRIBUTION LIST FOR ARCSL-TR-77059 (Contd)

Names	Copies	Names	Copies
Commander US Army Research Office - Durham Box CM, Duke Station Durham, NC 27706	1	Commander US Army Tank Automotive Command Attn: Code DRSTA-RHFL Warren, MI 48090	1
Advanced Research Projects Agency 1400 Wilson Boulevard Arlington, VA 22209	1	Weapons System: Evaluation Group Office of DDR&E 400 Army-Navy Drive Arlington, VA 22202	1
Atmospheric Sciences Laboratory		Commander	
Attn: DRSEL-BR-AS-P White Sands Missile Range, NM 88002	1	DARCOM, STITEUR Attn: DRXST-ST1 Box 48, APO New York 09710	1
Director			
Night Vision Laboratories Attn: DRSEL-NV-VI/Mr. R. Moulton Fort Belvoir, VA 23651	1	Commander US Army Science & Technology Center-Far Last Office APO San Francisco 96328	E
US Army Mobility Equipment Research and Development Center Attn: Code AMXFB-RCT/Mr. F. Keyer Fort Belvoir, VA 22060	1	US Public Health Service Room 18A-46 (CPT Osheroff) 5600 Fishers Lane Rockville, MD 20857	1